

In the Specification

Please replace the first full paragraph on page 1 with the following:

TECHNICAL FIELD

~~The present invention~~ This disclosure relates to a thermoplastic resin composition excellent in the balance between impact strength, particularly, impact strength at low temperatures, and fluidity as well as in the heat resistance, chemical resistance and paintability, and also relates to a shaped article thereof.

Please replace the second section title on page 1 with the following:

BACKGROUND ART

Please replace third full paragraph on page 2 with the following:

~~The present invention has been made~~ It could therefore be advantageous to solve those problems in the polyamide resin/rubber-reinforced styrene-based resin composition, and ~~an object of the present invention is~~ to provide a polyamide resin/rubber-reinforced styrene-based resin composition, particularly, a polyamide resin/ABS resin composition, excellent in balance between impact strength and fluidity as well as in heat resistance, chemical resistance and paintability.

Please replace the section title on page 2 and the paragraph spanning pages 2 through 5 with the following:

~~DISCLOSURE OF THE INVENTION~~ SUMMARY

~~According to the present invention, in order to attain the above described object, the following are provided. We thus provide:~~

- [1] A thermoplastic resin composition comprising the following components:
 - (A) from 20 to 79.5 parts by weight of a polyamide resin;
 - (B) from 20 to 79.5 parts by weight of a graft polymer,
the graft polymer being obtained by,
 - (a) in the presence of from 40 to 80 wt % of a rubber-like polymer having a swell index of 10 to 80 and a weight average particle diameter of 100 to 600 nm,
 - (b) graft-polymerizing from 20 to 60 wt % of a monomer mixture comprising:

(i) from 50 to 90 wt % of an aromatic vinyl-based monomer,
(ii) from 10 to 50 wt % of a vinyl cyanide-based monomer, and
(iii) from 0 to 30 wt % of another vinyl monomer copolymerizable with those monomers,

in which the acetone-soluble moiety of the graft polymer (B) has a number average molecular weight of 20,000 to 200,000;

(C) from 0.5 to 60 parts by weight of an unsaturated carboxylic acid-modified polymer, the unsaturated carboxylic acid-modified polymer being obtained by copolymerizing from 0.05 to 20 wt % of an unsaturated carboxylic acid monomer, from 50 to 89.95 wt % of an aromatic vinyl-based monomer and from 10 to 49.95 wt % of a vinyl cyanide-based monomer, and having a number average molecular weight of 22,000 to 60,000; and

(D) from 0 to 50 parts by weight of a copolymer, the copolymer being obtained by copolymerizing from 50 to 90 wt % of an aromatic vinyl monomer, from 10 to 50 wt % of a vinyl cyanide-based monomer and from 0 to 60 wt % of another vinyl-based monomer copolymerizable with those monomers;

with the proviso that the total amount of the components (A) to (D) is 100 parts by weight.

[2] A thermoplastic resin composition comprising the following components:

(A) from 20 to 79.5 parts by weight of a polyamide resin;

(B) from 20 to 79.5 parts by weight of a graft polymer, the graft polymer being obtained by,

(a) in the presence of from 40 to 80 wt % of a rubber-like polymer having a swell index of 10 to 80 and a weight average particle diameter of 100 to 600 nm,

(b) graft-polymerizing from 20 to 60 wt % of a monomer mixture comprising:

(i) from 50 to 90 wt % of an aromatic vinyl-based monomer,
(ii) from 10 to 50 wt % of a vinyl cyanide-based monomer, and
(iii) from 0 to 30 wt % of another vinyl monomer copolymerizable with those monomers,

in which the acetone-soluble moiety has a number average molecular weight of 20,000 to 200,000;

(C) from 0.5 to 60 parts by weight of an unsaturated carboxylic acid-modified polymer,

the unsaturated carboxylic acid-modified polymer being obtained by copolymerizing from 0.05 to 20 wt % of an unsaturated carboxylic acid monomer, from 50 to 89.95 wt % of an aromatic vinyl-based monomer and from 10 to 49.95 wt % of a vinyl cyanide-based monomer, and having a number average molecular weight of 22,000 to 60,000;

(D) from 0 to 50 parts by weight of a copolymer,

the copolymer being obtained by copolymerizing from 50 to 90 wt % of an aromatic vinyl monomer, from 10 to 50 wt % of a vinyl cyanide-based monomer and from 0 to 60 wt % of another vinyl-based monomer copolymerizable with those monomers;

with the proviso that the total amount of the components (A) to (D) is 100 parts by weight; and

(E) from 0.05 to 150 parts by weight of an inorganic filler.

[3] The thermoplastic resin composition as described in [2], wherein the number average molecular weight of the polyamide resin is from 10,000 to 20,000.

[4] The thermoplastic resin composition as described in any one of [1] to [3], wherein the graft polymer is obtained by graft-polymerizing styrene and acrylonitrile in the presence of a rubber-like polymer.

[5] The thermoplastic resin composition as described in [1] to [4], wherein the amount of the unsaturated carboxylic acid monomer in the unsaturated carboxylic acid-modified copolymer is from 0.5 to 10 wt %.

[6] The thermoplastic resin composition as described in [1] to [4], wherein the amount of the unsaturated carboxylic acid monomer in the unsaturated carboxylic acid-modified copolymer is from 0.8 to 7 wt %.

[7] The thermoplastic resin composition as described in [1] to [6], wherein the unsaturated carboxylic acid in the unsaturated carboxylic acid-modified copolymer is methacrylic acid.

[8] The thermoplastic resin composition as described in [1] to [7], wherein the unsaturated carboxylic acid-modified copolymer is obtained by copolymerizing methacrylic acid, styrene and acrylonitrile.

[9] The thermoplastic resin composition as described in [1] to [8], which comprises the rubber-like polymer in the range from 8 to 40 wt %.

[10] The thermoplastic resin composition as described in [1] to [8], which comprises the rubber-like polymer in the range from 10 to 25 wt %.

[11] The thermoplastic resin composition as described in [2] to [10], wherein the inorganic filler is a layered silicate with one unit having a one-side length of 0.002 to 1 μm and a thickness of 6 to 20 \AA .

[12] A shaped article comprising the thermoplastic resin composition described in [1] to [11].

[13] An automobile part obtained by shaping the thermoplastic resin composition described in [1] to [11].

Please replace the section title and the first, second and third full paragraphs on page 6 with the following:

~~MODE FOR CARRYING OUT THE INVENTION~~ DETAILED DESCRIPTION

Examples of the polyamide resin (A) ~~for use in the present invention~~ include nylon 6, nylon 46, nylon 66, nylon 69, nylon 610, nylon 612, nylon 116, nylon 4, nylon 7, nylon 8, nylon 11, nylon 12, nylon 6I, nylon 6/66, nylon 6T/6I, nylon 6/6T, nylon 66/6T, polytrimethylhexamethylene terephthalamide, polybis(4-aminocyclohexyl)methane dodecamide, polybis(3-methyl-4-aminocyclohexyl)methane dodecamide, polymetaxylylene adipamide, nylon 11T, polyundecamethylene hexahydroterephthalamide and polyamide elastomer. In these examples, I represents an isophthalic acid component and T represents a terephthalic acid component. Among these, nylon 6, nylon 46, nylon 66, nylon 12, nylon 6T/6I, nylon 6/6T and nylon 66/6T are preferred.

In the case where an inorganic filler is contained, the polyamide resin (A) ~~for use in the present invention~~ has a number average molecular weight of 10,000 to 20,000. If the number average molecular weight is less than 10,000, the impact strength disadvantageously decreases, whereas if the number average molecular weight exceeds 20,000, the fluidity disadvantageously decreases.

In the thermoplastic resin composition ~~of the present invention~~, the polyamide resin (A) is used in an amount of 20 to 79.5 parts by weight, preferably from 20 to 70 parts by weight, with the proviso that the total amount of the components (A) to (D) is 100 parts by weight. If the amount of the polyamide resin is less than 20 parts by weight, poor chemical resistance results, whereas if it exceeds 79.5 parts by weight, the impact strength decreases.

~~In the present invention, the~~ The graft polymer (B) is a polymer obtained by graft-polymerizing from 60 to 20 wt % of a monomer mixture comprising from 90 to 50 wt % of an aromatic vinyl-based monomer, from 10 to 50 wt of a vinyl cyanide-based monomer and from 0 to 30 wt % of another vinyl monomer copolymerizable with those monomers in the presence of from 40 to 80 wt % of a rubber-like polymer having a swell index of 10 to 80 and a weight average particle diameter of 100 to 600 nm, in which the acetone-soluble moiety of the graft polymer (B) has a number average molecular weight of 20,000 to 200,000.

Please replace the third full paragraph on page 8 with the following:

~~According to the present invention, the~~ The graft polymer (B) can be obtained by graft-polymerizing an aromatic vinyl-based monomer, a vinyl cyanide-based monomer and if desired, another vinyl monomer copolymerizable with these monomers to the above-described rubber-like polymer. Examples of the aromatic vinyl-based monomer include styrene, α -methylstyrene, p-methylstyrene, chlorostyrene and bromostyrene. These monomers are used individually or as a mixture of two or more thereof. Among these, styrene and α -methylstyrene are preferred. Examples of the vinyl cyanide-based monomer include acrylonitrile and methacrylonitrile. These monomers are also used individually or as a mixture of two or more thereof. In particular, acrylonitrile is preferred.

Please replace the paragraph spanning pages 8 and 9 with the following:

~~According to the present invention, the~~ The rubber-like polymer in the thus-obtained graft polymer (B) has a swell index of 10 to 80, preferably from 15 to 50, more preferably from 25 to 45. The swell index is a value measured and calculated as follows. That is, a latex is coagulated and dried, about 1 g of the polymer is then precisely weighed, immersed in about 50 g of toluene and left standing at 23°C for 48 hours to swell the polymer, and thereafter extra toluene is removed by decantation. The swelled polymer is precisely weighed without delay and then dried under reduced pressure at 80°C for 24 hours. After the absorbed toluene is removed by evaporation, the polymer is again precisely weighed, and the swell index is calculated according to the following formula.

Please replace the second and third full paragraphs on page 9 with the following:

~~In the present invention, if~~ If the swell index of the rubber-like polymer for use in the production of the graft polymer (B) is less than 10 or exceeds 80, the impact strength of the thermoplastic resin composition obtained is extremely low.

~~According to the present invention, the~~ The weight average particle diameter of the rubber-like polymer in the graft polymer (B) is preferably from 100 to 600 nm, more preferably from 150 to 450 nm. ~~In the present invention, it~~ It is preferred that a diene-based rubber latex particle comprising the rubber polymer having the above-described swell index and weight average particle diameter is obtained by various methods as described later and in the presence of this diene-based rubber latex particle as-is or after enlargement by aggregation, those aromatic vinyl-based monomer and vinyl cyanide-based monomer are graft-polymerized to obtain the graft polymer. For enlarging the diene-based rubber latex particle by aggregation, as is well known, the particles may be mechanically aggregated or an acidic substance may be added to the latex.

Please replace the paragraph spanning pages 9 and 10 with the following:

~~According to the present invention, the~~ The acetone-soluble moiety in the graft polymer (B) has a number average molecular weight of 20,000 to 200,000. If the number average molecular weight of the acetone-soluble moiety in the graft polymer is less than 20,000, the thermoplastic resin composition obtained suffers from poor impact strength, whereas if it exceeds 200,000, the thermoplastic resin composition obtained exhibits poor fluidity. ~~In the present invention, the~~ The number average molecular weight of the acetone-soluble moiety in the graft polymer is preferably from 20,000 to 100,000, more preferably from 20,000 to 60,000.

Please replace the three full paragraphs on page 10 with the following:

~~In the present invention, the~~ The method for producing such a graft polymer is not particularly limited and a conventionally known method may be used. For example, an emulsion polymerization method, a suspension polymerization method, a bulk polymerization method, a solution polymerization method or a combination thereof may be appropriately used.

~~In the thermoplastic resin composition of the present invention,~~ the graft polymer (B) is used in an amount of 20 to 79.5 parts by weight, preferably from 20 to 70 parts by weight, with the

proviso that the total amount of the components (A) to (D) is 100 parts by weight. If the amount used is less than 20 parts by weight, the impact strength decreases, whereas if it exceeds 79.5 parts by weight, the fluidity decreases.

~~According to the present invention, the~~ The unsaturated carboxylic acid-modified copolymer (C) is a copolymer obtained by copolymerizing from 0.05 to 20 wt %, preferably from 0.5 to 10 wt %, more preferably from 0.8 to 7 wt % of an unsaturated carboxylic acid monomer, from 89.95 to 50 wt %, preferably 89.5 to 55 wt %, more preferably from 84.2 to 60 wt % of an aromatic vinyl-based monomer, and from 10 to 49.95 wt %, preferably from 10 to 44.5 wt %, more preferably from 15 to 39.2 wt % of a vinyl cyanide-based monomer, and has a number average molecular weight of 22,000 to 60,000, preferably from 25,000 to 60,000.

Please replace the two full paragraphs on page 11 with the following:

~~In the present invention, a~~ A part of the aromatic vinyl-based monomer constituting the unsaturated carboxylic acid-modified copolymer (C) can be replaced by another vinyl-based monomer copolymerizable with the aromatic vinyl-based monomer, for example, by an unsaturated carboxylic acid ester-based monomer such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate and 2-ethylhexyl acrylate.

~~According to the present invention, the~~ The unsaturated carboxylic acid-modified copolymer must have a number average molecular weight of 22,000 to 60,000 so as to obtain a resin composition excellent in the balance between impact strength and fluidity. If the number average molecular weight of the unsaturated carboxylic acid-modified copolymer (C) is less than 22,000, the resin composition obtained is inferior in chemical resistance or paintability, whereas if it exceeds 60,000, the resin composition obtained exhibits poor fluidity. Here, the number average molecular weight of the unsaturated carboxylic acid-modified copolymer (C) is a molecular weight determined by dissolving the copolymer in tetrahydrofuran and measuring its molecular weight according to the GPC method (gel permeation chromatography method).

Please replace the two full paragraphs on page 12 with the following:

The unsaturated carboxylic acid-modified copolymer (C) is contained in an amount of 0.5 to 60 parts by weight, preferably from 1 to 35 parts by weight, with the proviso that the total of the

components (A) to (D) in the thermoplastic resin composition of the present invention is 100 parts by weight. If the amount of the unsaturated carboxylic acid-modified copolymer (C) is less than 0.5 parts by weight, this copolymer is not uniformly dispersed in the resin composition and the obtained resin composition is inferior in the impact strength and paintability, whereas if it exceeds 60 parts by weight, the obtained resin composition exhibits poor fluidity.

~~According to the present invention, the~~ The unsaturated carboxylic acid-modified copolymer (C) having a number average molecular weight of 22,000 to 60,000 and containing from 0.05 to 20 wt % of an unsaturated carboxylic acid monomer is blended in the resin composition within an appropriate range, whereby excellent compatibility can be obtained between the polyamide resin and the styrene-based resin, and a thermoplastic resin composition excellent in the balance between impact strength and fluidity, particularly excellent in the impact strength at low temperatures, can be obtained.

Please replace the first and third full paragraphs on page 13 with the following:

~~In the present invention, the~~ The copolymer (D) is a copolymer obtained by copolymerizing from 90 to 50 wt % of an aromatic vinyl-based monomer, from 10 to 50 wt % of a vinyl cyanide-based monomer and from 0 to 60 wt % of another vinyl monomer copolymerizable with those monomers. The copolymer (D) is preferably a copolymer obtained by copolymerizing from 90 to 55 wt % of an aromatic vinyl-based monomer, from 10 to 45 wt % of a vinyl cyanide-based monomer and from 0 to 10 wt % of another vinyl monomer copolymerizable with those monomers.

~~In the present invention, the~~ The weight average molecular weight of the copolymer (D) is not particularly limited but is usually from 50,000 to 250,000, preferably from 55,000 to 200,000. This copolymer (D) can be obtained by a conventionally known appropriate method such as an emulsion polymerization method, a bulk polymerization method, a suspension polymerization method and a solution polymerization method.

Please replace the paragraph spanning pages 13 and 14 with the following:

In the thermoplastic resin composition of the present invention, the copolymer (D) is used in an amount of 0 to 50 parts by weight, preferably from 1 to 35 parts by weight, with the proviso that

the total amount of the components (A) to (D) is 100 parts by weight. If the amount used exceeds 50 parts by weight, the impact strength decreases.

Please replace the first full paragraph on page 14 with the following:

As described above, the thermoplastic resin composition of the present invention comprises from 20 to 79.5 parts by weight of the polyamide resin (A), from 20 to 79.5 parts by weight of the graft polymer (B), from 0.5 to 60 parts by weight of the unsaturated carboxylic acid-modified copolymer (C) and from 0 to 50 parts by weight of the copolymer (D) (with the proviso that the total of the components (A) to (D) is 100 parts by weight). If any one component departs from this range, a thermoplastic resin composition having desired properties cannot be obtained.

Please replace the paragraph spanning pages 14 and 15 with the following:

Furthermore, in the present invention, the content of the rubber-like polymer occupying in the entire resin composition is preferably from 8 to 40 wt %, more preferably from 10 to 25 wt %, in view of balance in physical properties of the thermoplastic resin composition obtained.

Please replace the first full paragraph on page 15 with the following:

The inorganic filler (E) used in one preferred embodiment of the present invention includes a fibrous or non-fibrous inorganic filler. Specific examples thereof includes may include fibrous fillers such as glass fiber, carbon fiber, potassium titanate whisker, zinc oxide whisker, aluminum borate whisker, aramid fiber, alumina fiber, silicon carbide fiber, ceramic fiber, asbestos fiber, gypsum fiber and metal fiber, and non-fibrous fillers such as silicates (e.g., wollastonite, zeolite, sericite, kaolin, mica, clay, pyrophyllite, bentonite, montmorillonite, asbestos, talc, aluminosilicate), metal oxides (e.g., alumina, silicon oxide, magnesium oxide, zirconium oxide, titanium oxide, iron oxide), carbonates (e.g., calcium carbonate, magnesium carbonate, dolomite), sulfates (e.g., calcium sulfate, barium sulfate), hydroxides (e.g., magnesium hydroxide, calcium hydroxide, aluminum hydroxide), glass beads, ceramic beads, boron nitride, silicon carbide and silica. These inorganic fillers may have a hollow shape and may be used in combination of two or more thereof. From the standpoint of obtaining more excellent mechanical strength, such a filler is preferably used after preliminarily treating it with a coupling agent such as an isocyanate-based compound, an acryl-based compound,

an organic silane-based compound, an organic titanate-based compound, an organic borane-based compound and an epoxy compound.

Please replace the paragraph spanning pages 15 and 16 with the following:

The amount used of the inorganic filler (E), ~~for use in the present invention~~, is from 0.05 to 150 parts by weight per 100 parts by weight of the thermoplastic resin comprising the components (A), (B), (C) and (D). If the amount used is less than 0.05 parts by weight, the effect of enhancing the mechanical strength and heat resistance is small, whereas if it exceeds 150 parts by weight, the shapability or surface state disadvantageously changes for the worse. In the case of using a fibrous filler as the inorganic filler (E), the amount used is preferably from 5 to 100 parts by weight.

Please replace the first full paragraph on page 16 with the following:

A layered silicate may also be used as the inorganic filler (E) ~~for use in the present invention~~. When a layered silicate is used, an effect of enhancing the mechanical strength and heat resistance can be obtained by the addition in a small amount and therefore, the fluidity or surface property is improved.

Please replace the paragraph spanning pages 17 and 18 with the following:

As described above, the thermoplastic resin composition ~~of the present invention~~ comprises 100 parts by weight of the thermoplastic resin comprising from 79.5 to 20 parts by weight, preferably from 70 to 20 parts by weight of the polyamide resin (A), from 20 to 79.5 parts by weight, preferably from 20 to 70 parts by weight of the graft polymer (B), from 0.5 to 60 parts by weight, preferably from 1 to 35 parts by weight of the unsaturated carboxylic acid-modified copolymer (C) and from 0 to 50 parts by weight, preferably from 1 to 35 parts by weight of the copolymer (D) (with the proviso that the total of (A), (B), (C) and (D) is 100 parts by weight), and from 0.05 to 150 parts by weight of the inorganic filler (E). If any one component departs from this range, a thermoplastic resin composition having desired properties cannot be obtained. Particularly, ~~in the present invention~~, the content of the rubber-like polymer occupying in the entire resin composition is preferably from 8 to 40 wt % in view of balance in physical properties of the thermoplastic resin composition obtained.

Please replace the first full paragraph on page 18 with the following:

The thermoplastic resin composition of the present invention can be obtained by uniformly melt-mixing the above-described polyamide resin (A), graft polymer (B), unsaturated carboxylic acid-modified copolymer (C) and copolymer (D) and, if desired, further the inorganic filler (E), but the mixing order thereof is not particularly limited. For example, all components may be en bloc mixed at the same time, or after any two components are preliminarily mixed, remaining components may be added thereto and mixed. At the time of melt-mixing the mixture of respective components, an extruder, a Banbury mixer, a roll mill or the like may be used.

Please replace the first two full paragraphs on page 19 with the following:

~~According to the present invention, a~~ A shaped article is obtained by shaping the thermoplastic resin composition described above. As for the shaping method, a commonly employed shaping method such as injection molding, extrusion molding, blow molding, vacuum molding and press molding can be used. In particular, injection molding and extrusion molding are preferred. The thus-obtained shaped article may be subjected to a secondary processing such as coating, vapor deposition and adhesion.

The shaped article of the present invention is excellent in the impact strength, heat resistance, chemical resistance and paintability and can be used for electric-electronic parts, machine parts and automobile parts such as automobile functional parts, automobile interior parts and automobile exterior parts. In particular, the shaped article of the present invention is suitably used for automobile parts.

Please replace the paragraph spanning 19 and 20 with the following:

EXAMPLES

~~The present invention is~~ Our resins and compositions are described below by referring to Examples, but ~~the present invention is~~ they are not limited thereto. In Examples, the "parts" and "%" are on a weight basis.

Please replace the two paragraphs on page 34 with the following:

INDUSTRIAL APPLICABILITY

As described in the foregoing pages, the thermoplastic resin composition ~~of the present invention~~ comprises a polyamide resin, a rubber-reinforced styrene-based resin, an unsaturated carboxylic acid-modified copolymer as a compatibilizing agent and, if desired, an aromatic vinyl-based monomer-vinyl cyanide-based monomer copolymer and, if desired, further comprises an inorganic filler, and by using, particularly, a polyamide resin having a number average molecular weight within the specified range, a rubber-reinforced styrene-based resin with the acetone-soluble moiety having a number average molecular weight within the specified range, and an unsaturated carboxylic acid-modified copolymer having a number average molecular weight within a predetermined range, the thermoplastic resin composition ~~of the present invention~~ can be excellent in the balance between impact strength and fluidity and also excellent in the heat resistance, chemical resistance and paintability.

Accordingly, the shaped article comprising the thermoplastic resin composition ~~of the present invention~~ can be used for electric and electronic parts, machine parts, automobile parts such as automobile functional parts, automobile interior parts and automobile exterior parts. In particular, the shaped article ~~of the present invention~~ can be suitably used for automobile parts.